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NO_2^+ AS A CONSTITUENT OF THE D REGION

by

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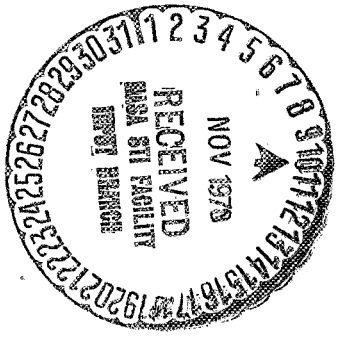
The purpose of this letter is to discuss the processes which will lead to NO_2^+ as a constituent of the D region. The results of a recent measurement of the ionization potential of NO_2 by Natalis and Collin (1968) shows the IP to be 8.8eV (1409A) as compared with the usually accepted value of 9.75eV Dibeler, et al. (1967). The difference is attributed to ions formed in a vibrationally excited state. The lower ionization potential allows the NO_2 present in the mesosphere to be ionized by the solar Lyman-α line at 1215.6A as well as other wavelengths shorter than 1409A.

For wavelengths longer than 1369A the O_2 absorption cross section is (1-1.5) X 10^{-17} cm^2 so that radiation is absorbed above 100 km. Between 1369A and 1340A, the onset of NO ionization, the O_2 absorption cross section decreases to 2.2 X 10^{-18} cm^2. Nitrogen absorption is negligible throughout the wavelength interval, Watanabe (1958). In the case of NO Lyman-α is the dominant source of ionization. Therefore, assuming NO_2 to have an



ionization cross-section equivalent to that for NO, $2 \times 10^{-18} cm^2$, the ion pair production function will be

$$q_{NO_2} = q_{NO} \frac{NO_2}{NO}$$

The distribution of NO_2 is considered to be determined by the processes, Nicolet (1955, 1965).

$$NO + O \rightarrow NO_2 \rightarrow h\nu \quad k_1$$

$$NO + O + M \rightarrow NO_2 + M \quad k_2$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad k_3$$

$$NO_2 + h\nu \rightarrow NO + O \quad J_{NO_2}$$

$$NO_2 + O \rightarrow NO + O_2 \quad k_4$$

Under equilibrium conditions this gives

$$\frac{[NO_2]}{NO} = \frac{k_1[O] + k_2[O]\,[M] + k_3\,[O_3]}{J_{NO_2} + k_4\,[O]}$$

A value $[NO_2]/[NO] \sim 10^{-3}$ in the 70 to 85 km altitude region during the day is in good agreement with a complete computer solution of the equations by Keneshea and Fowler (1966). The usually quoted lifetime of NO_2 is 200 seconds and it will behave like ozone and atomic oxygen so that there will be an increase during the night and solar eclipses. At the end of the night the ratio $[O_3]/[O]$ is 10^4 at 70 km and unity at 80 km.

The $[NO_2]$ density will exceed the NO density in the lower mesosphere. An exact solution of the equations involved should be undertaken for any thorough study of the nocturnal NO_2 distribution.

It is also possible that the reaction

$$NO^+ + NO_2 \rightarrow NO_2^+ + NO + 1eV$$

will occur. The rate coefficient should be in the $10^{-10} cm^3 sec^{-1}$ range. Because of the low concentration of NO_2 this reaction will probably have a small effect on the distribution of NO^+ during the day. It could be very important below 80 km at night. Shahin (1966) has observed $NO_2^+ (H_2O)_n$ in laboratory experiments. Ions of this sort may be present in the D region for sufficient quantities of H_2O. If H_2O is insufficient then mass 46^+ should be a component of the ions measured by direct sampling of the D region. Varney and Gunton, 1969, quote Narcisi as having detected mass 46^+ as a minor species of ion at 80 km. In laboratory experiments Varney and Gunton (1969) report the formation of NO_2^+ in air. The lower ionization potential of the molecule and the tendency to form vibrationally excited ions will assist in explaining their results.

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